



Advanced Electrochemical Energy Storage Devices

NASA's Intramural Technology Project

Developments in Li-Ion and Li-CF_x Batteries

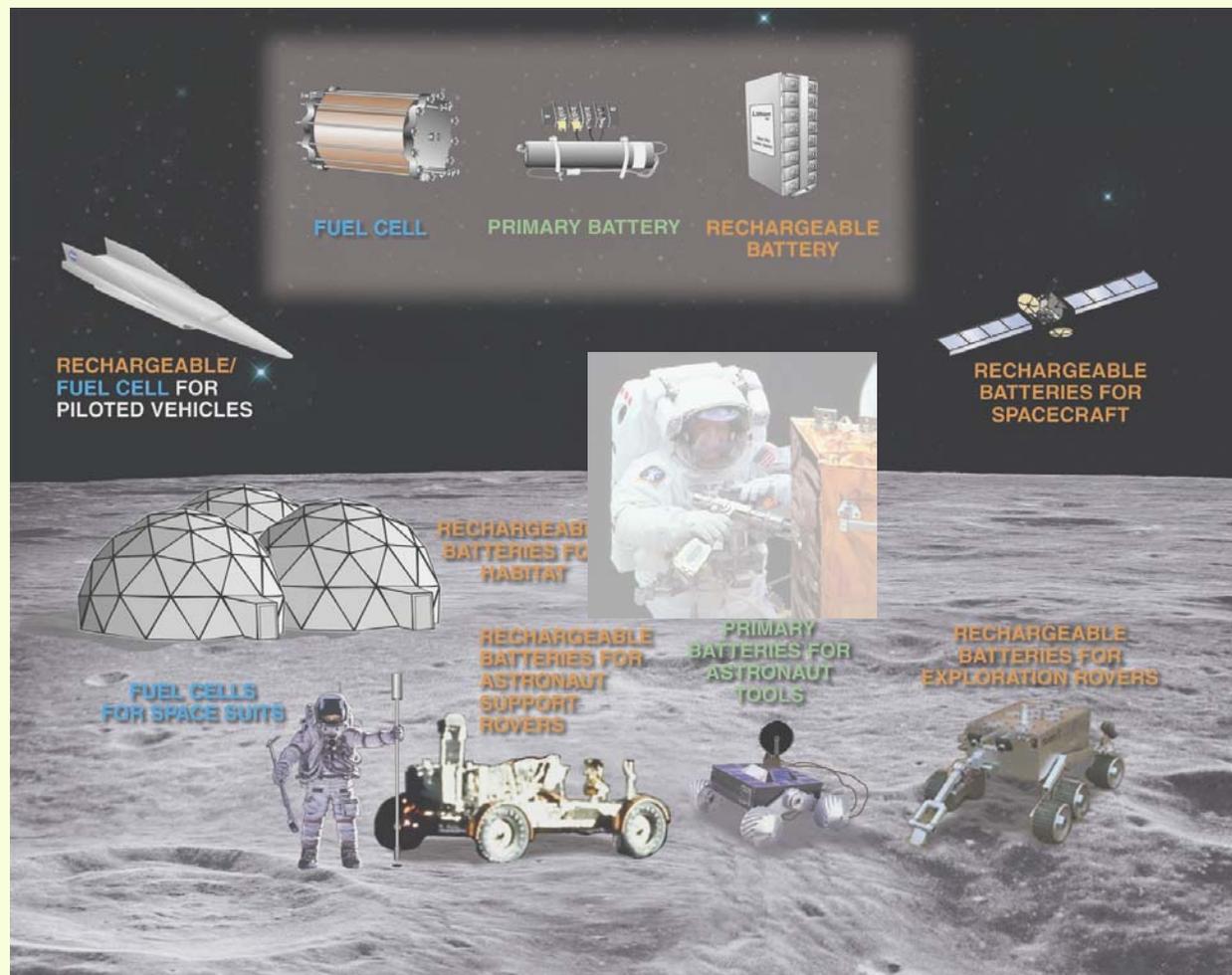
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*NASA Battery Workshop, Huntsville, AL,
Dec. 1, 2005*



Electrochemical Energy Storage Devices In Robotic and Human Exploration Missions

- **Robotic Exploration**
 - Rechargeable batteries for **Rovers, Landers and Orbiters**
 - Primary batteries for **Rovers and Probes**
- **Human Exploration**
 - Primary batteries for **Astronaut tools and planetary probes**
 - Rechargeable batteries for **Rovers, Landers, Habitat and Extra vehicular Activities**
 - Fuel cells for **Pressurized rovers, EVA and habitats**





Energy Storage Needs for Robotic and Human Exploration Missions

- **Planetary Rovers and Landers**
 - High specific energy and energy density
 - Wide operating temperature
 - Moderate cycle Life.
 - Safety
- **Planetary probes**
 - High specific energy and energy density
 - Wide operating temperature
- **Habitats and Planetary Stations for Sustained Exploration**
 - High specific energy and energy density
 - Long cycle life
 - Calendar life (5-10 years)
- **Extra Vehicular activities (space suits, tools)**
 - High specific energy and energy density
 - safety



Advanced Electrochemical Energy Storage Devices



OBJECTIVE

Develop advanced energy storage devices and demonstrate their performance capabilities for ESMD Missions

- Rechargeable Li-Ion batteries (> 160 Wh/kg & -60°C)
- Li primary batteries (> 400 Wh/kg & -60°C)
- Compact, H₂-O₂ Fuel Cell system (200W) (> 500 Wh/kg)

APPROACH

- Demonstrate feasibility of advanced materials (Year-1)
- Select/develop advanced materials (Year-2)
- Fabricate prototype cells and demo. performance (Year-3)
- Fabricate batteries and demonstrate performance (Year 4)

DELIVERABLES:

- **Phase-I:** Concept feasibility studies on adv. materials
- **Phase-II:** Engineering models of Li-ion and Li primary cells and batteries, fuel cells stacks and systems.

ESMD Mission Applications (Spiral 2 & Beyond)

- Advanced rechargeable batteries for mobile systems, Extra Vehicular Activities (EVA), and Astronaut equipment and Surface systems.
- Advanced primary batteries for Extra Vehicular Activities (EVA), and Astronaut equipment, and
- Compact Fuel cells for mobile systems, human rovers and Extra vehicular Activities.

ADVANTAGES OVER SOA

- 2-3 fold mass and volume reduction and Lower operating temperatures (to -60°C) for primary and rechargeable batteries.
- Two fold benefit in mass and volume and scalability for small fuel cell applications.

TEAM:

Project Lead: R. Bugga (NASA-JPL)

Partnering Organizations:

- NASA-JPL
- NASA Centers: GRC, MSFC and JSC
- Universities: UT Austin, CIT and USC
- Industry:

BUDGET

Element	Ph-I	Ph-II-Y1	Ph-II-Y2	Ph-II-Y3	Total
Management	106	215	260	247	828
Adv. Rechargeable Li-Ion	677	1612	1892	1621	5803
Adva. Primary Li	412	984	1132	1051	3580
Adv. PEM Fuel Cell	428	1012	1214	1403	4057
Total	1623	3823	4498	4322	14267



Technology Metrics and Demonstrations



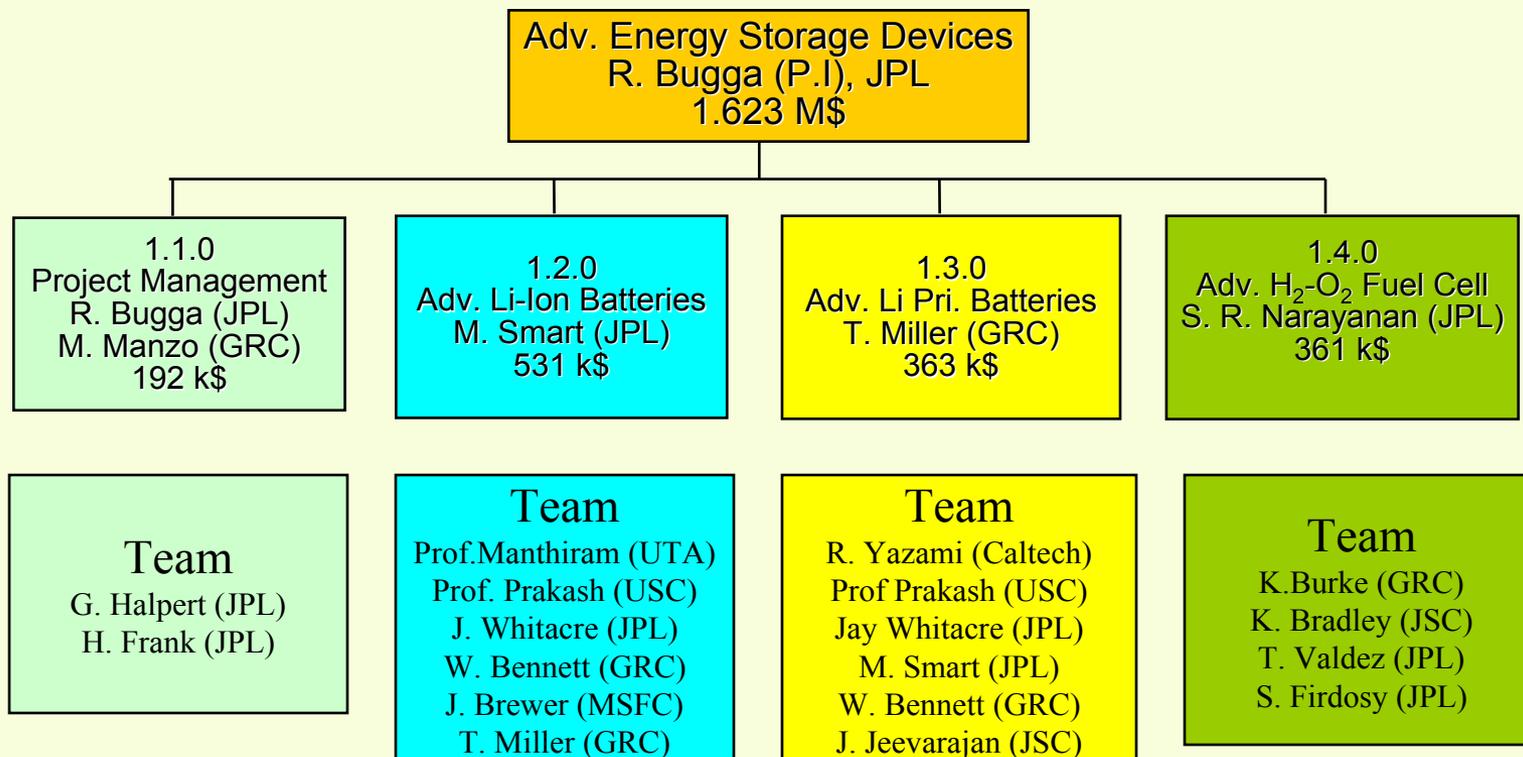
Energy storage System	Phase-I Year-1	Phase-II Year-1	Phase-II Year-2	Phase-II Year-3
Demo System	Lab Cell	Lab Cell	EM Cells	EM Battery
Advanced Rechargeable- Li-ion batteries	200 mAh/g cathode; -40 C Operation	250 mAh/g cathode; - 60 C operation	200 Wh/kg cell 500 Wh/l -60 to 60 C > 10 years	160 Wh/kg* battery 320 Wh/l* -60 to 60 C > 10 years
Advanced Lithium Primary	> C/20 rate and 600mAh/g cathode -40 C Operation	> C/10 rate & 800mAh/g -60 C Operation	500 Wh/kg; 1000 Wh/l; > C/10 rate -60 °C to +60°C 10 years life	400 Wh/kg battery; 800 Wh/l; > C/10 rate -60 °C to +60°C 10 years life
Demo System	Cell	Cell	FC Stack	FC system
PEM Fuel Cell	400 mW/cm ² 60% Efficiency	600 mW/cm ² 65% eff.	500 W/kg 65% efficiency	200 W/kg@ 60% eff > 500 Wh/kg >10 years



PHASE I PROJECT WORK BREAKDOWN STRUCTURE AND OBJECTIVES



Advanced Electrochemical Energy Storage Devices





Materials for Advanced Li-Ion Batteries

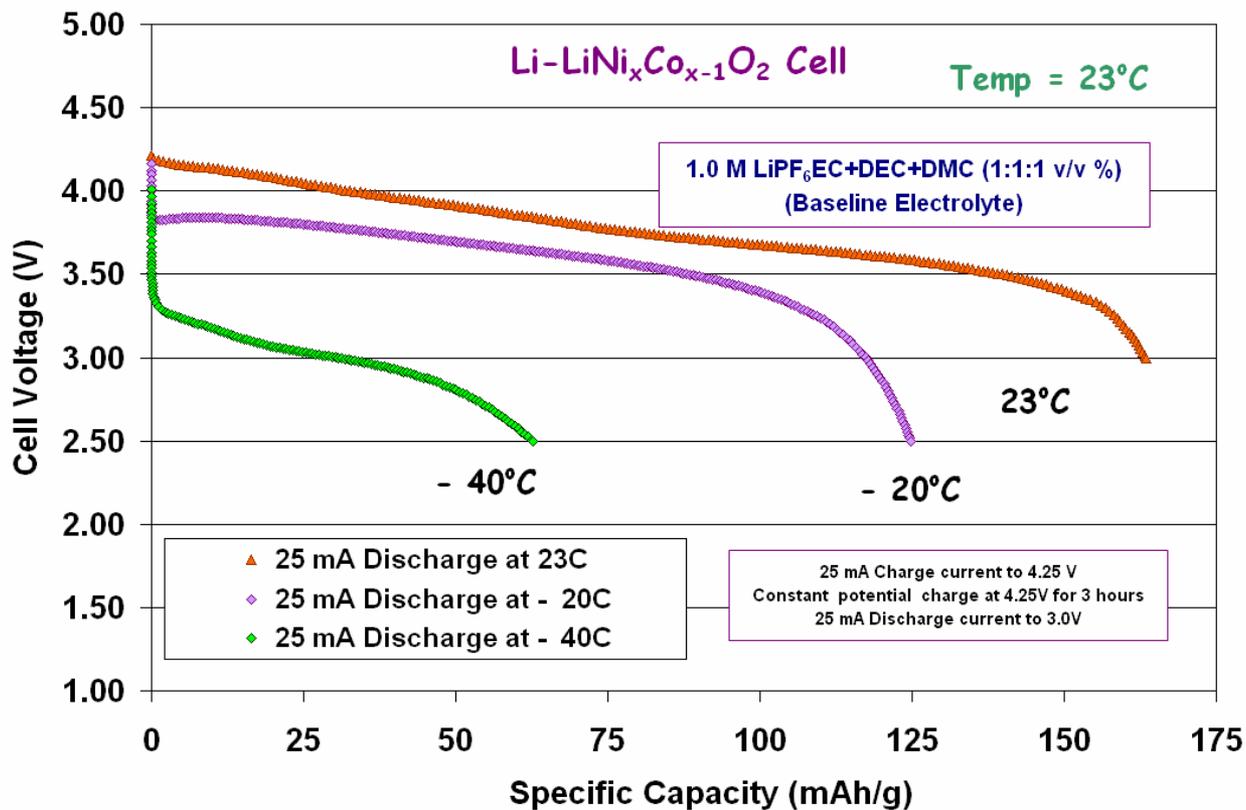


Material	Cathodes Layered Mixed metal oxides		Electrolytes (Carbonate based mixed solvents)	
	Composition	Source	Composition	Source
SOA	$\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$	<ul style="list-style-type: none">• Yardney electrodes• OMG powder	1.0 M LiPF ₆ in 1:1:1 EC+DMC+DEC	USC/JPL
Gen 1	$\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	<ul style="list-style-type: none">• Synthesized at JPL	1.0 M LiPF ₆ in 1:1:1:3 EC+DMC+DEC+EMC	USC/JPL
Gen-2	$\text{Li}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})\text{O}_2$	<ul style="list-style-type: none">• UTA Powder• DoE and Enax electrodes• Max Power cells	1.0 M LiPF ₆ in EC+EMC with fluorinated co-solvents and 2) 1:4 EC+EMC	USC/JPL
Gen 3	$\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	<ul style="list-style-type: none">• UTA Powder	1.0 M LiPF ₆ in 1:4 EC+EMC mixtures with fluorinated co- solvents	USC/JPL

Tested in coin cells or glass cylindrical (jelly roll) cells



SOA Li-Ion Cathodes $\text{Li/LiNi}_x\text{Co}_{1-x}\text{O}_2$ in SOA Electrolytes Half Cell Results Cylindrical Cells



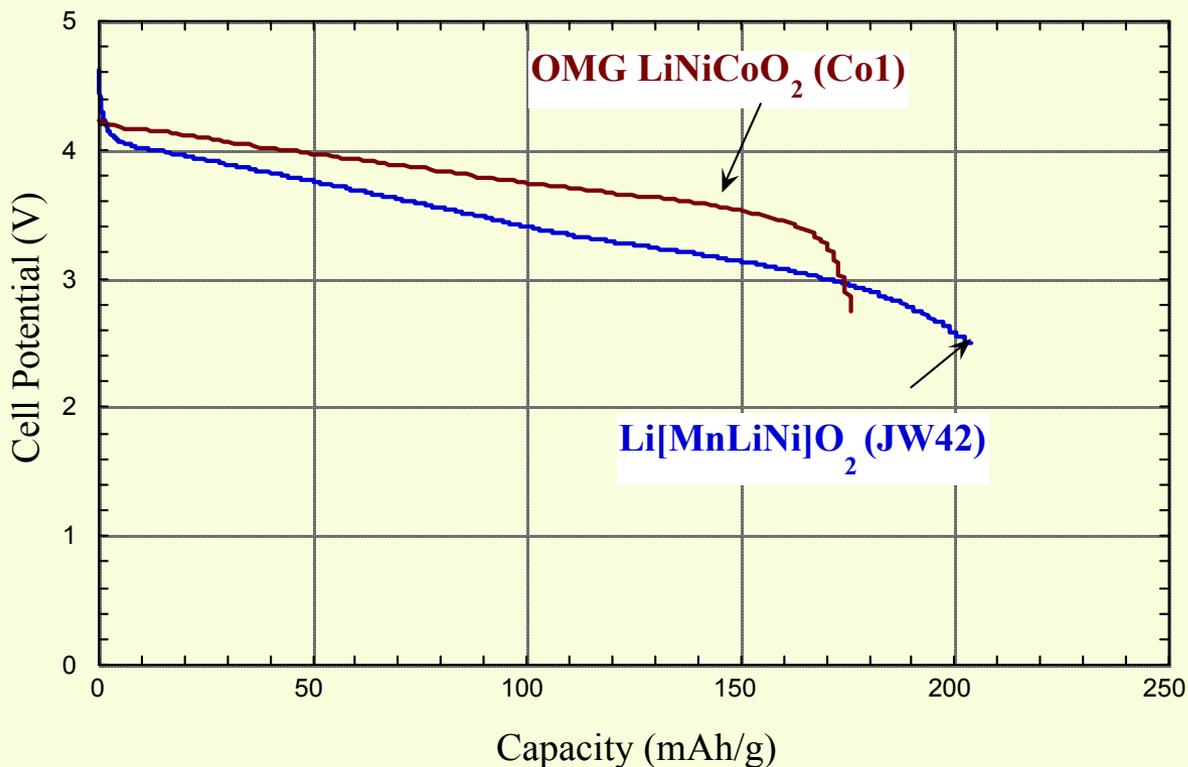
Baseline Electrolyte = 1.00 M LiPF₆ EC+DEC+DMC (1:1:1 v/v %)

- ~ 70% Capacity at -20°C and 25% at -40°C with baseline electrolyte.



Generation-1 Cathode $\text{Li}(\text{Mn}_{0.61}\text{Li}_{0.21}\text{Ni}_{0.18})\text{O}_2$

Comparison of Standard OMG LiNiCoO_2 with JPL-Fabricated $\text{Li}[\text{MnLiNi}]\text{O}_2$ Cathode Material, Third Discharge



- Higher initial capacities (>200 mAh/g) at high charge voltages, but accompanied by faster capacity decay



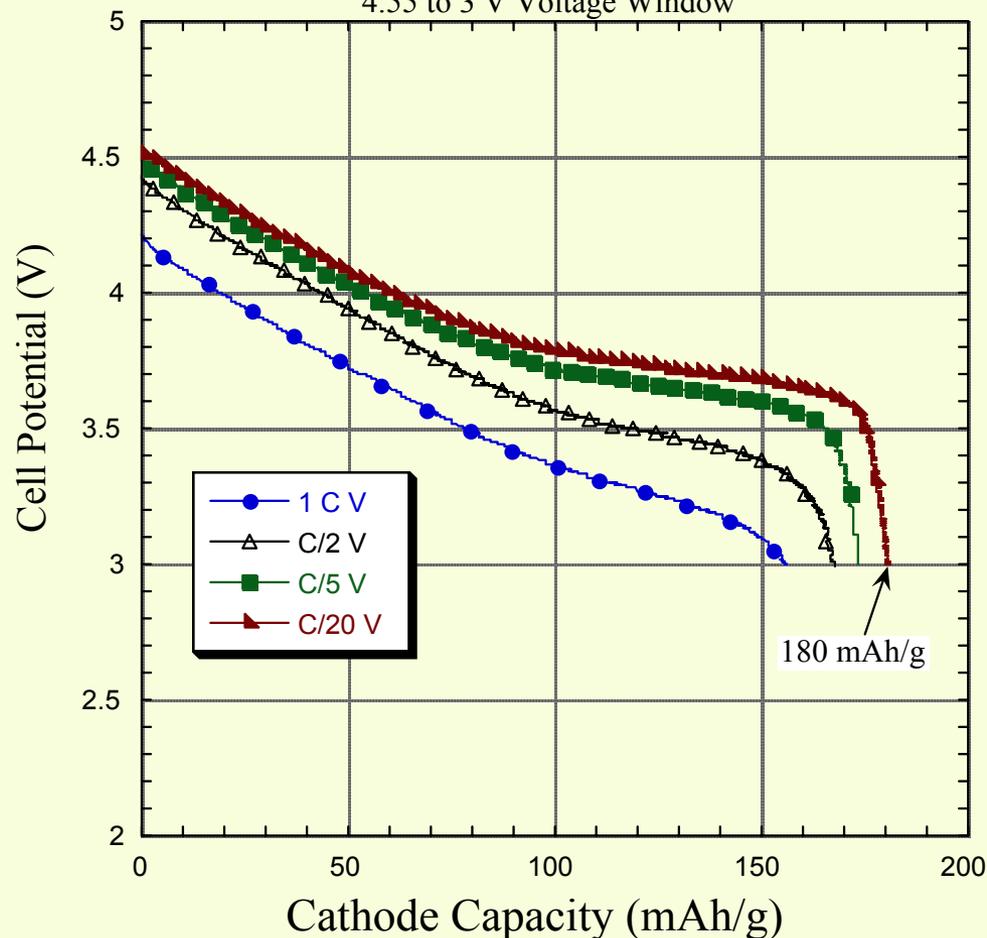
Generation-2 Cathode $\text{Li}(\text{Mn}_{0.33}\text{Co}_{0.33}\text{Ni}_{0.33})\text{O}_2$



1/3, 1/3, 1/3 "Gen 2" layered cathode material
from UT Austin, First Cycle

Rate Capability Study

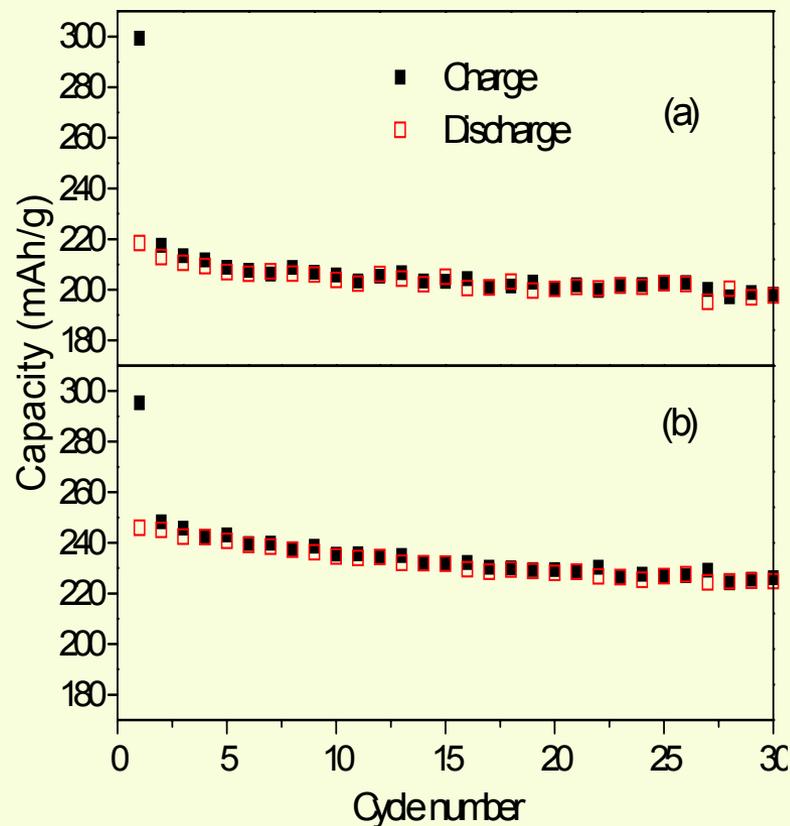
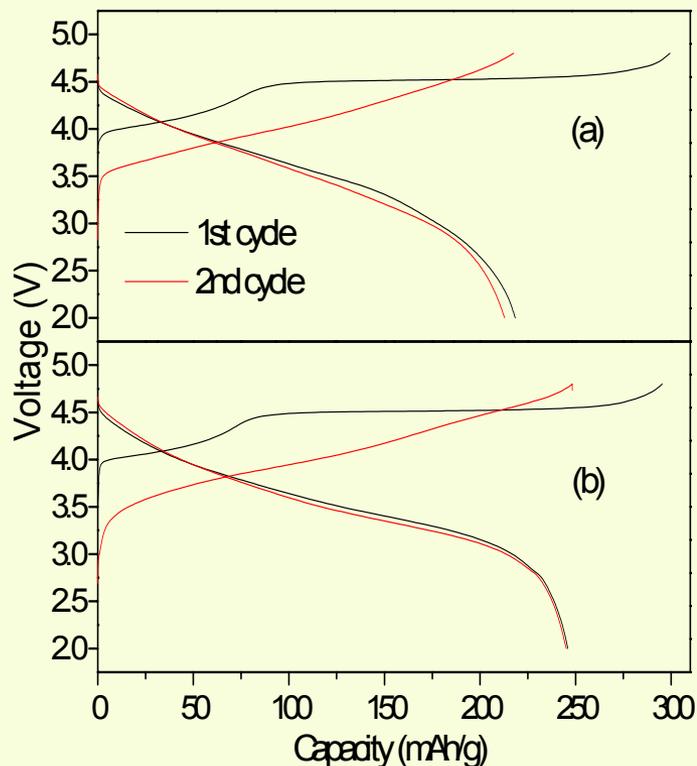
~0.021g active material, 16 mm diameter active area
4.55 to 3 V Voltage Window



- **180 mAh/g with Gen-2 Cathode at 25°C**



Gen-III Cathode Material (UTA)

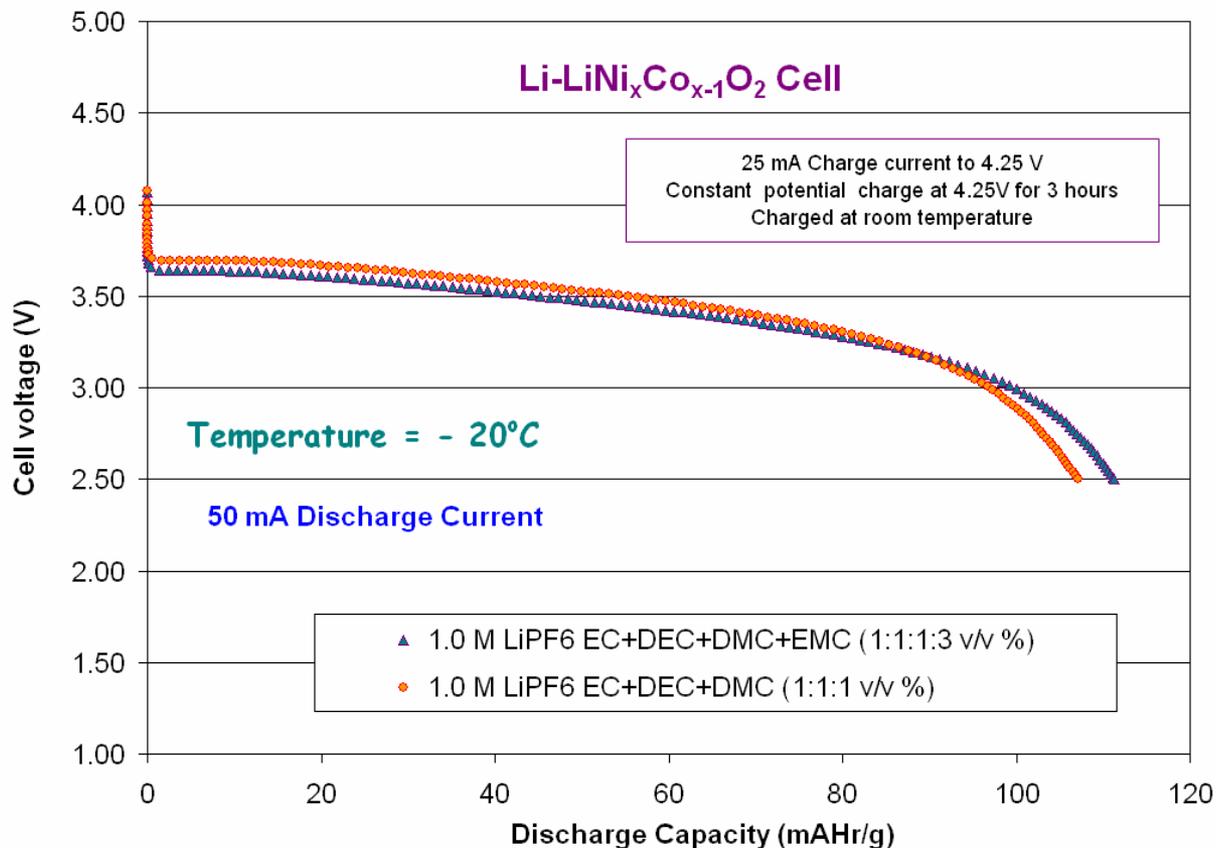


To be Published by Manthiram et al

Comparison of the charge-discharge profiles (first 2 cycles) and cyclability of (a) unmodified and (b) modified layered $\text{Li}(\text{Li},\text{Co},\text{Ni},\text{Mn})\text{O}_2$ cathodes (sample 1).



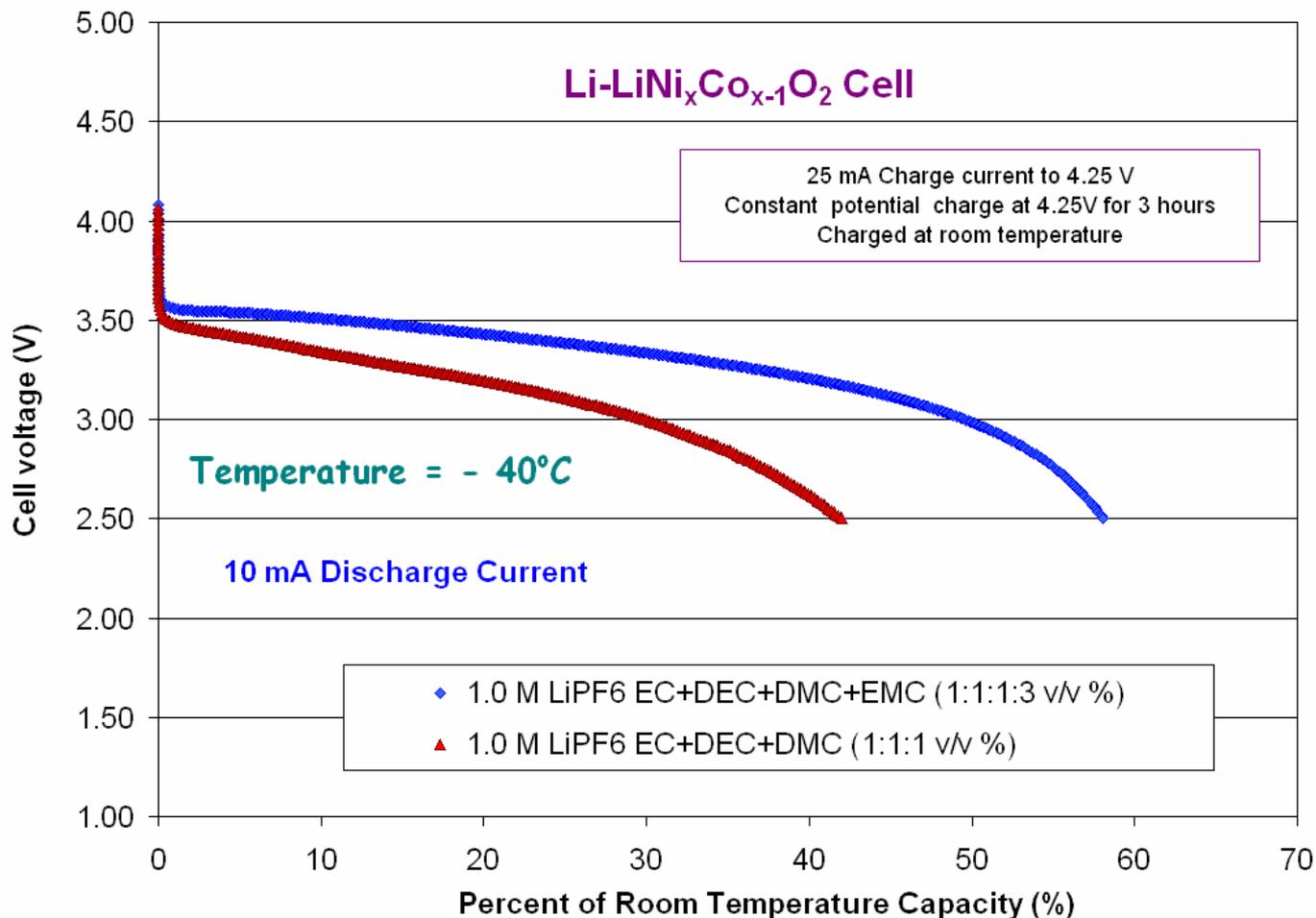
Generation -1 Electrolyte at -20°C with Li/LiNi_xCo_{1-x}O₂ cathode Half Cell Results



- Similar performance at -20°C of Baseline Electrolyte: 1.00 M LiPF₆ EC+DEC+DMC (1:1:1 v/v %) and Gen I Electrolyte = 1.00 M LiPF₆ EC+DEC+DMC+EMC (1:1:1:3 v/v %)



Generation -1 Electrolyte at -40°C with Li/LiNi_xCo_{1-x}O₂ cathode Half Cell Results

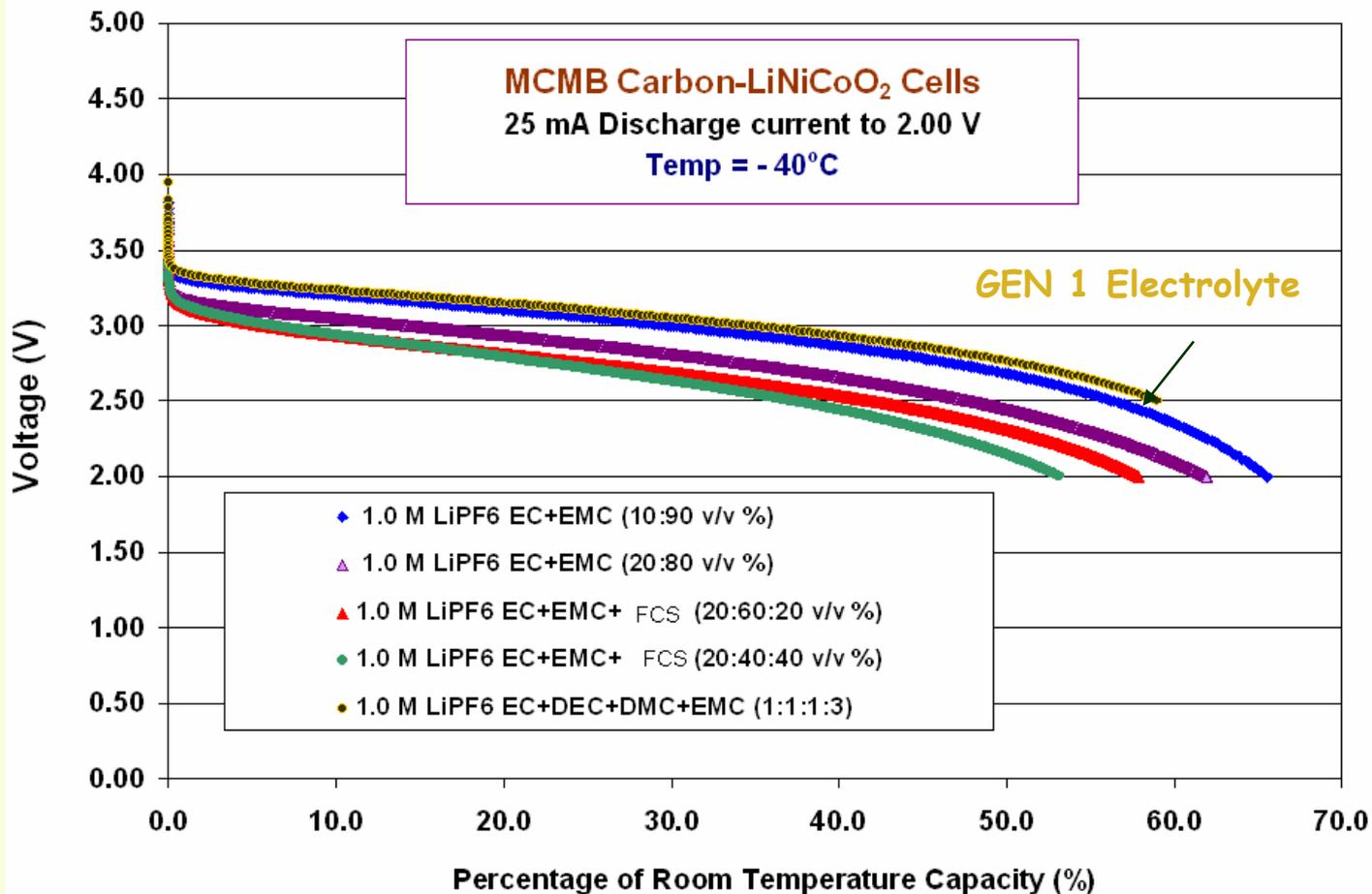


- Improved performance at -40°C compared to the baseline electrolyte



Gen 2 Electrolytes at Low Temperatures

Evaluation of Electrolytes with Fluorinated co-solvents



- 25 mA Discharge to 2.00 V (~ C/14 Discharge Rate)
- Performance similar to Gen-1, but with the advantage of non-flammability



Formation Characteristics of Graphite-LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ Cells

Evaluation of Carbonate-Based Low Temperature Electrolytes

(Electrodes Supplied by Argonne National Lab.)

			1.0 M LiPF ₆ in EC+EMC (20:80 v/v %)		1.2 M LiPF ₆ in EC+EMC (20:80 v/v %)		1.2 M LiPF ₆ in EC+EMC (30:70 v/v %)	
Temperature (°C)	Current (mA)	Rate	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)	Capacity (Ah)	Percent (%)
23°C	25.00	C/5	0.13582	100.00	0.13911	100.00	0.12652	100.00
- 40°C	6.25	C/20	0.08337	61.38	0.08163	58.68	0.08181	64.66
	8.33	C/15	0.08172	60.17	0.08193	58.89	0.07946	62.80
	12.50	C/10	0.07891	58.10	0.08029	57.72	0.07365	58.21
	25.00	C/5	0.07089	52.19	0.07503	53.94	0.04636	36.64
	41.67	C/3	0.03462	25.49	0.03609	25.94	0.01732	13.69
- 50°C	62.50	C	0.01394	10.26	0.01618	11.63	0.01110	8.77
	6.25	C/20	0.05091	37.48	0.05421	38.97	0.04468	35.31
	8.33	C/15	0.03605	26.54	0.04065	29.22	0.03216	25.42
	12.50	C/10	0.02613	19.24	0.03546	25.49	0.01651	13.05
	25.00	C/5	0.01188	8.74	0.01325	9.53	0.00528	4.17

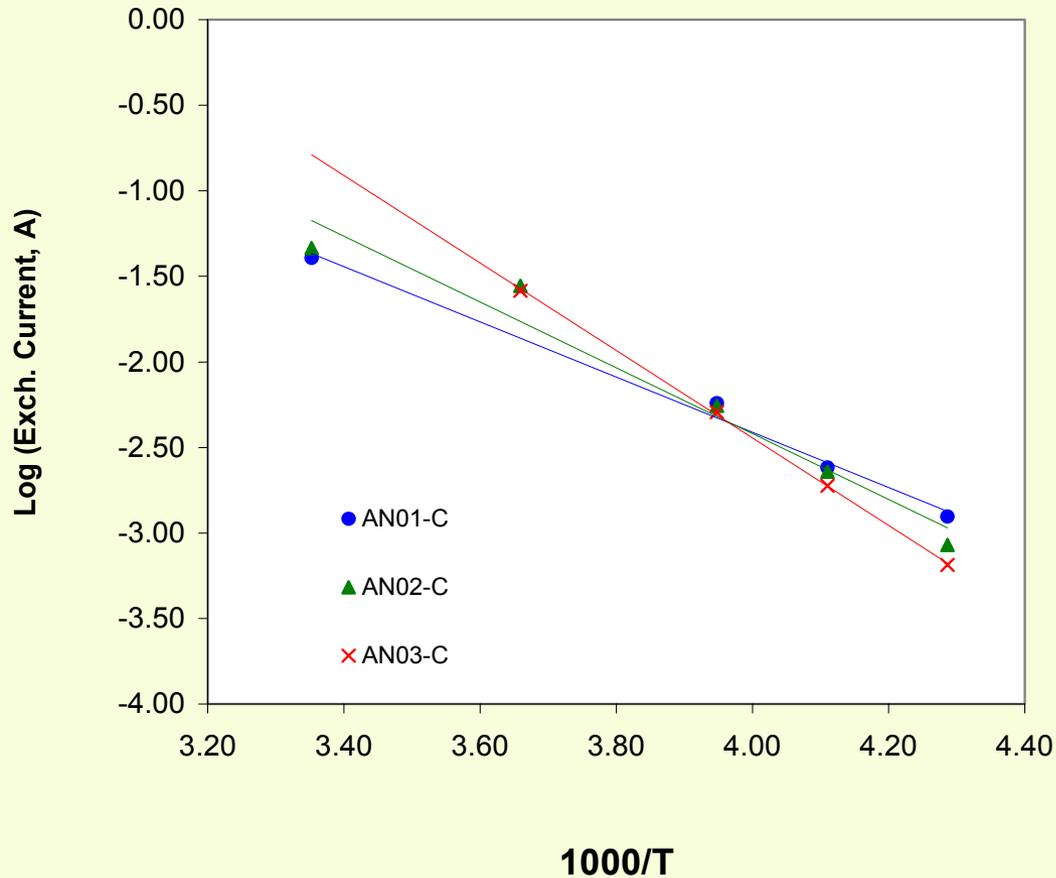
➤ Cells charged at room temperature (23°C, C/5 rate to 4.30V) prior to discharge.



Cathode Kinetics in the Three Different Electrolytes



Cathode Exchange Currents from Tafel



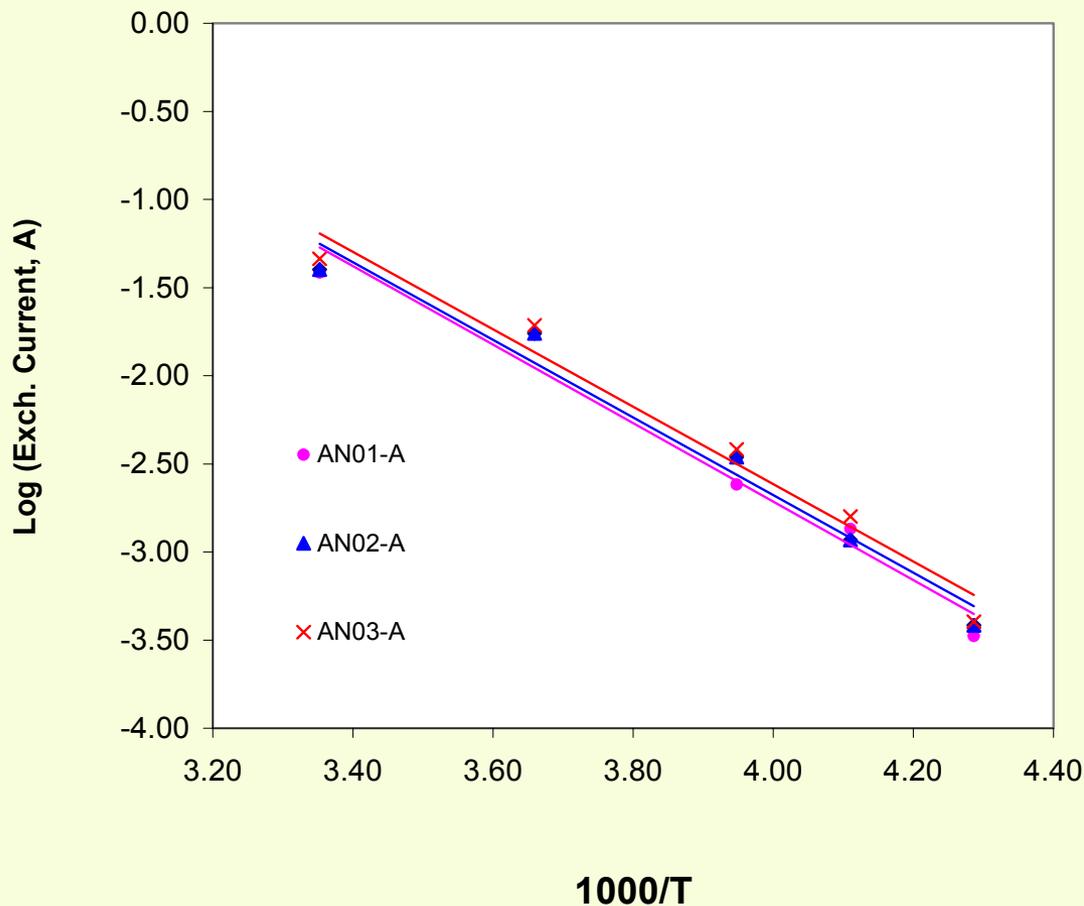
- Similar trend in the kinetics as the discharge performance



Anode Kinetics in the Three Different Electrolytes



Anode Exchange Currents from Tafel



- The anode kinetics also decrease with temperatures, but at the same rate in the three electrolytes.
- Similar behavior observed in the kinetics from EIS and DC Micropolarization.



Comparison of SOA, Gen-1, Gen-2 and Gen-3 Materials

Goals: 180 mAh/g Phase-1 and > 200 mAh/g Phase-II

Cathode	Composition	Performance Summary
SOA	Layered- $\text{Li}(\text{Ni}_{0.8}\text{Co}_{0.2})\text{O}_2$	<ul style="list-style-type: none"> • ~165 mAh/g when charged to 4.1 V. • Low irreversible capacity (< 30 mAh/g) & Good Cycle life
Generation 1	Layered $\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	<ul style="list-style-type: none"> • > 200 mAh/g when charged to 4.6 V. • High irrev. Cap. (> 30% mAh/g)? Rapid fade at high Voltage
Generation-2	Layered- $\text{Li}(\text{Ni}_{0.33}\text{Co}_{0.33}\text{Mn}_{0.33})\text{O}_2$	<ul style="list-style-type: none"> ➢ 180 mAh/g reversible capacity ➢ 30 mAh/g of Irrev. capacity and good cyclability
Generation 3	Layered $\text{Li}(\text{Mn,Ni,Co,Li})\text{O}_2$	<ul style="list-style-type: none"> ➢ 240 mAh/g reversible capacity ➢ 30 mAh/g of Irrev. capacity and good cyclability

Goals: -40°C Phase-1 and -60°C Phase-II

Electrolyte	Composition	Performance Summary
SOA	1.0 M LiPF_6 in 1:1:1 EC+DMC+DEC	<ul style="list-style-type: none"> • Good for -20°C. (70% capacity) • Good Cycle life and calendar life
Generation 1	1.0 M LiPF_6 in 1:1:1:3 Ec+DMC+DEC+EMC	<ul style="list-style-type: none"> • Good for -40°C. (70% capacity) • Good Cycle life and calendar life
Generation-2 and Generation-3	1.0 M LiPF_6 in EC+EMC mixtures with fluorinated co-solvents	<ul style="list-style-type: none"> • Good for -40°C. (70% capacity) • Non flammability



Materials for Advanced Li-CF_x Batteries



Material	Cathodes Carbon Sub-fluorides		Electrolytes (PC based mixed solvents)	
	Composition	Source	Composition	Source
SOA	CF _x (x=1.0 to 1.08)	<ul style="list-style-type: none">• EPI Electrodes• Rayovac powder• Daikeen powder	1.0 LiBF ₄ in 1:1 PC+DME	USC/JPL
Gen 1	CF _{0.53}	<ul style="list-style-type: none">• CNRS(France)/ Caltech	1.0 LiBF ₄ in 1:4 PC+DME	USC/JPL
Gen-2	CF _{0.64}	CNRS(France)/ Caltech	1.0 LiBF ₄ in PC+DME with fluorinated co-solvents	USC/JPL
Gen 3	CF _x from MWCNT	CNRS(France)/ Caltech	1.0 LiBF ₄ in PC+DME with fluorinated co-solvents	USC/JPL

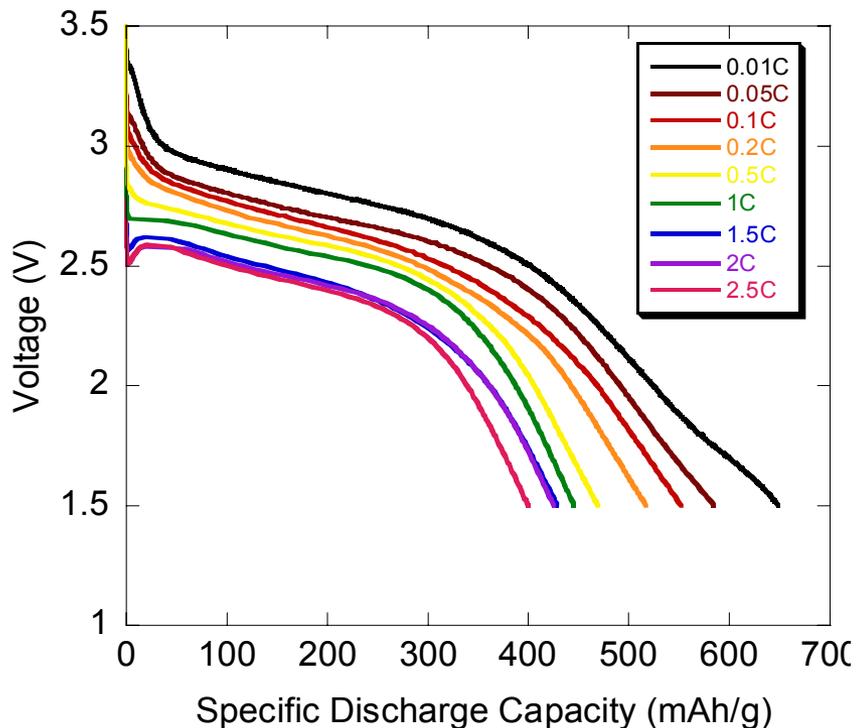
Tested in coin cells or glass cylindrical (jelly roll) cells



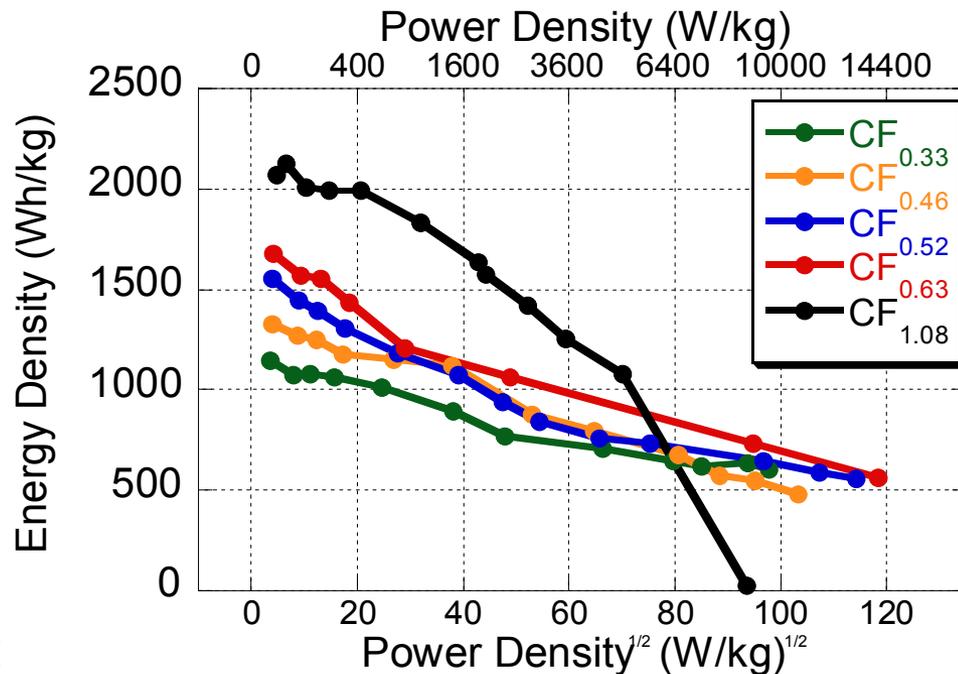
Earlier Data

(From Prof Humwi and Dr Yazami)

Rate Capability of CF_{0.52}



Ragone plot of CF_x cathodes

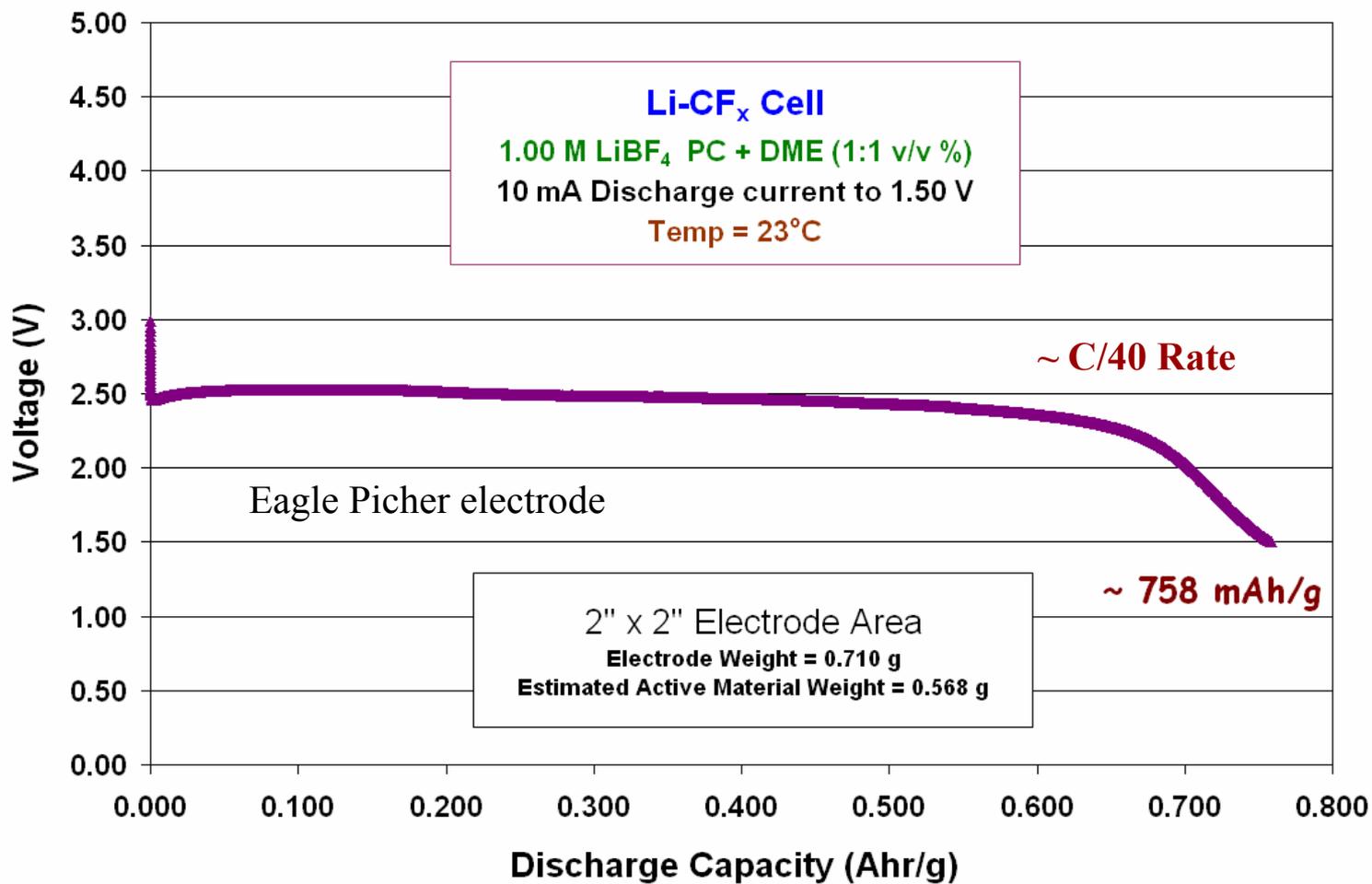


x in (CF _x) _n	0.25	0.33	0.50	0.66	1.00
Theoretical Capacity (mAh/g)	400	484	623	721	864

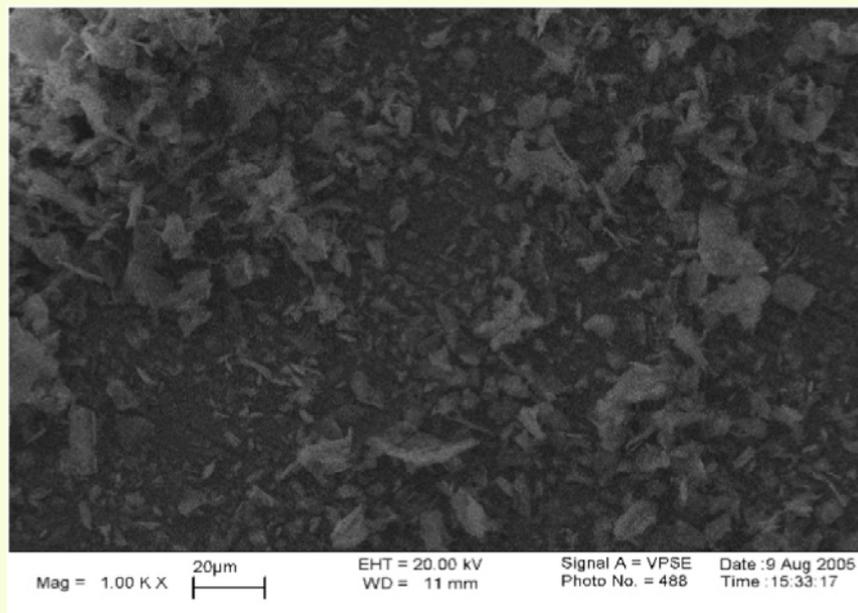
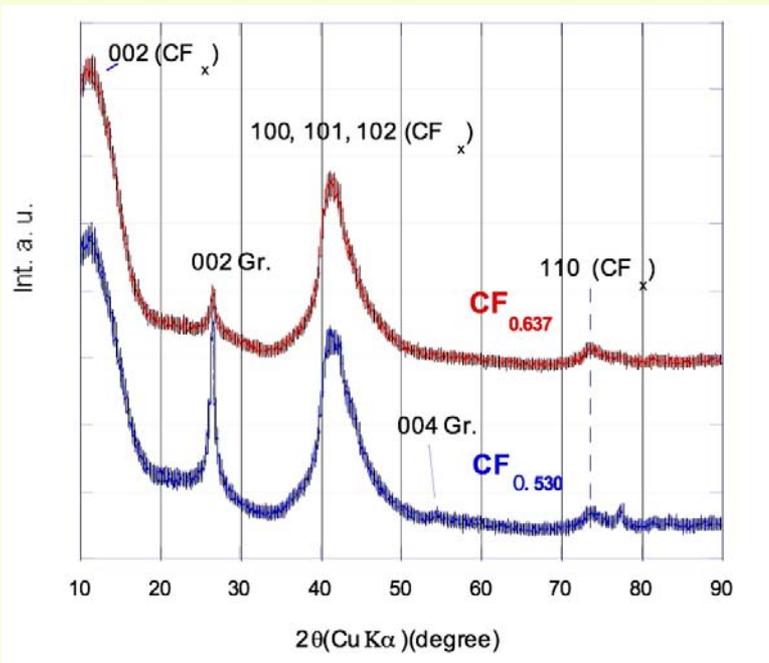


Lithium- CF_x Experimental Cell Results

Discharge Performance at Room Temperature



Carbon Subfluorides from Caltech

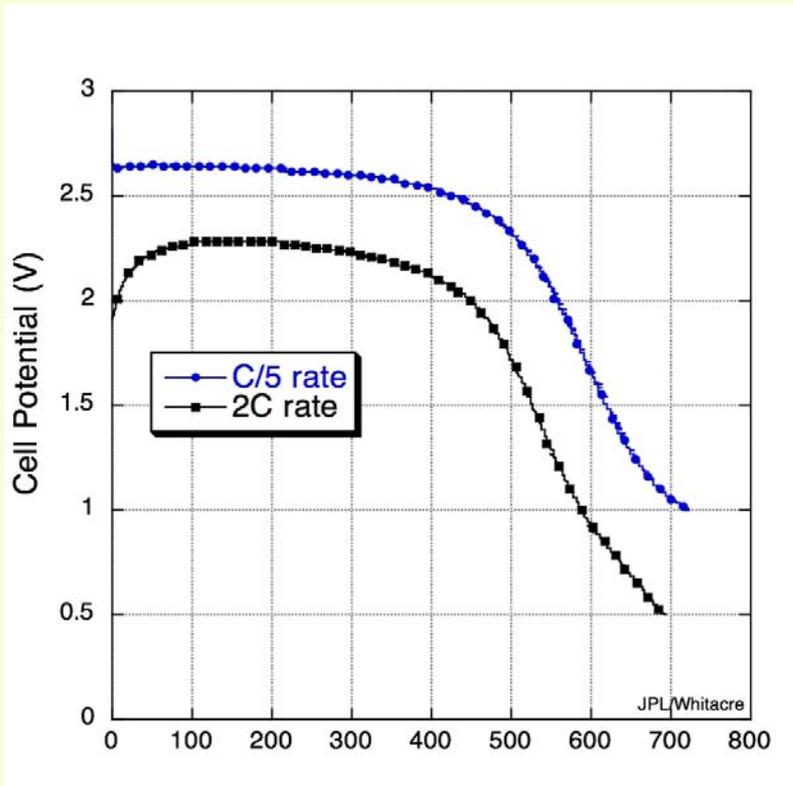


- Both graphite and Carbon monofluoride present
- No staging.

- Similar microstructure on graphite as well as carbon monofluoride; flakes of 1-10 microns dia.



Room Temperature Performance of $\text{CF}_{0.64}$

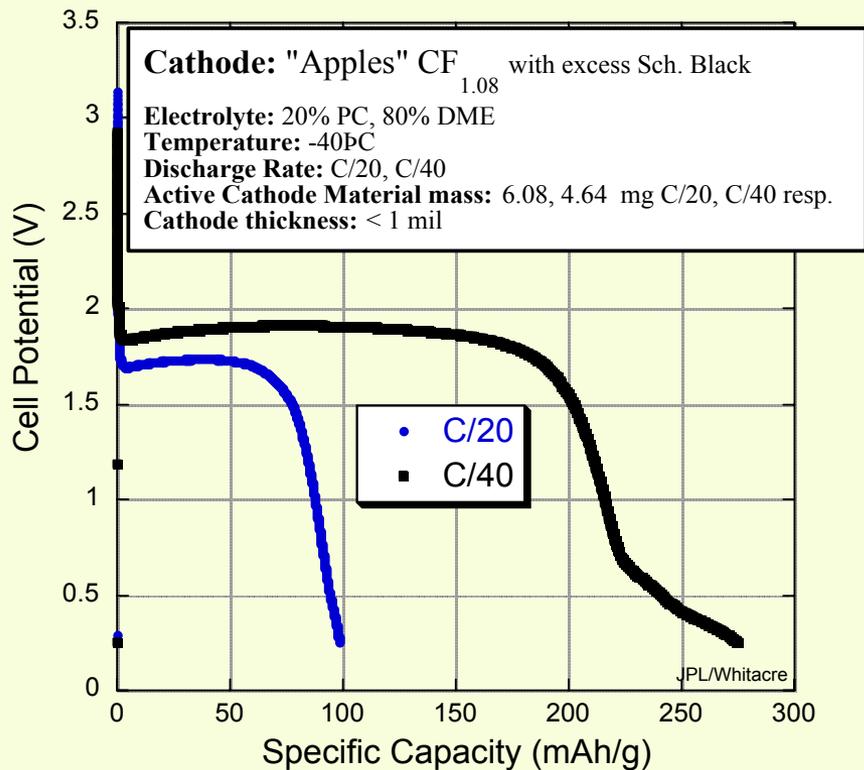


- High discharge rates possible (Electrode 103 mil thick).
- Results consistent with previous observations

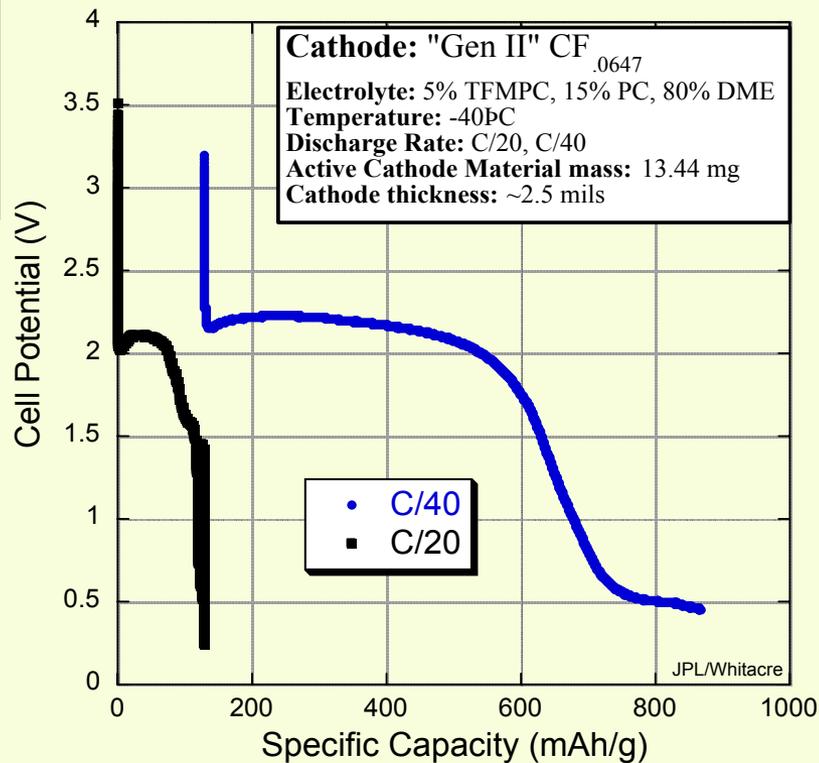


Comparison of Baseline vs. Gen-2 Cathode at -40°C

Baseline (with excess C)



Gen-2 CF_{0.64}

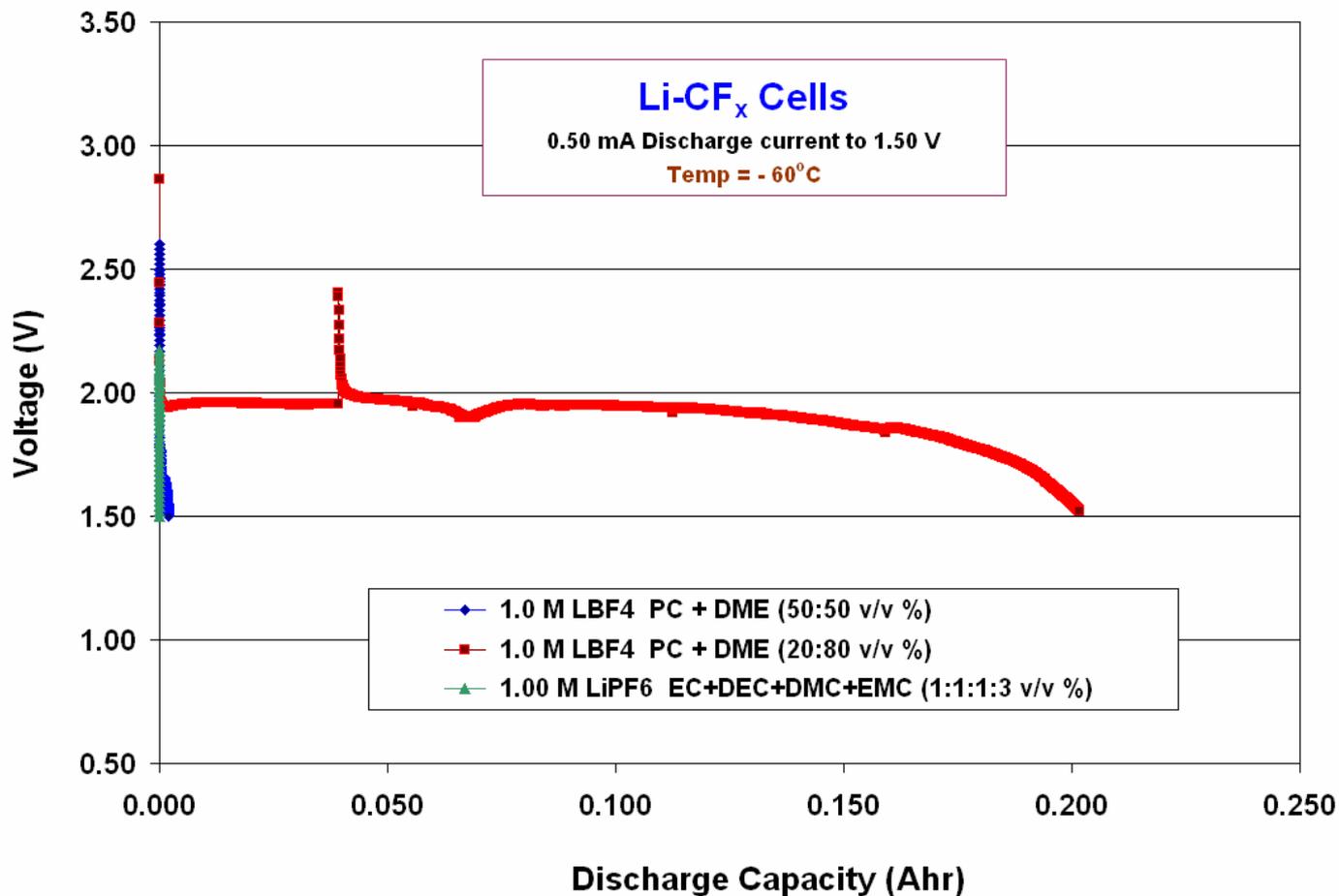


- Higher capacity with subfluorides compared to the baseline electrode (thinner!) containing equivalent carbon diluent



Gen-1 Electrolytes for Lithium-CF_x

Discharge Performance at -60°C

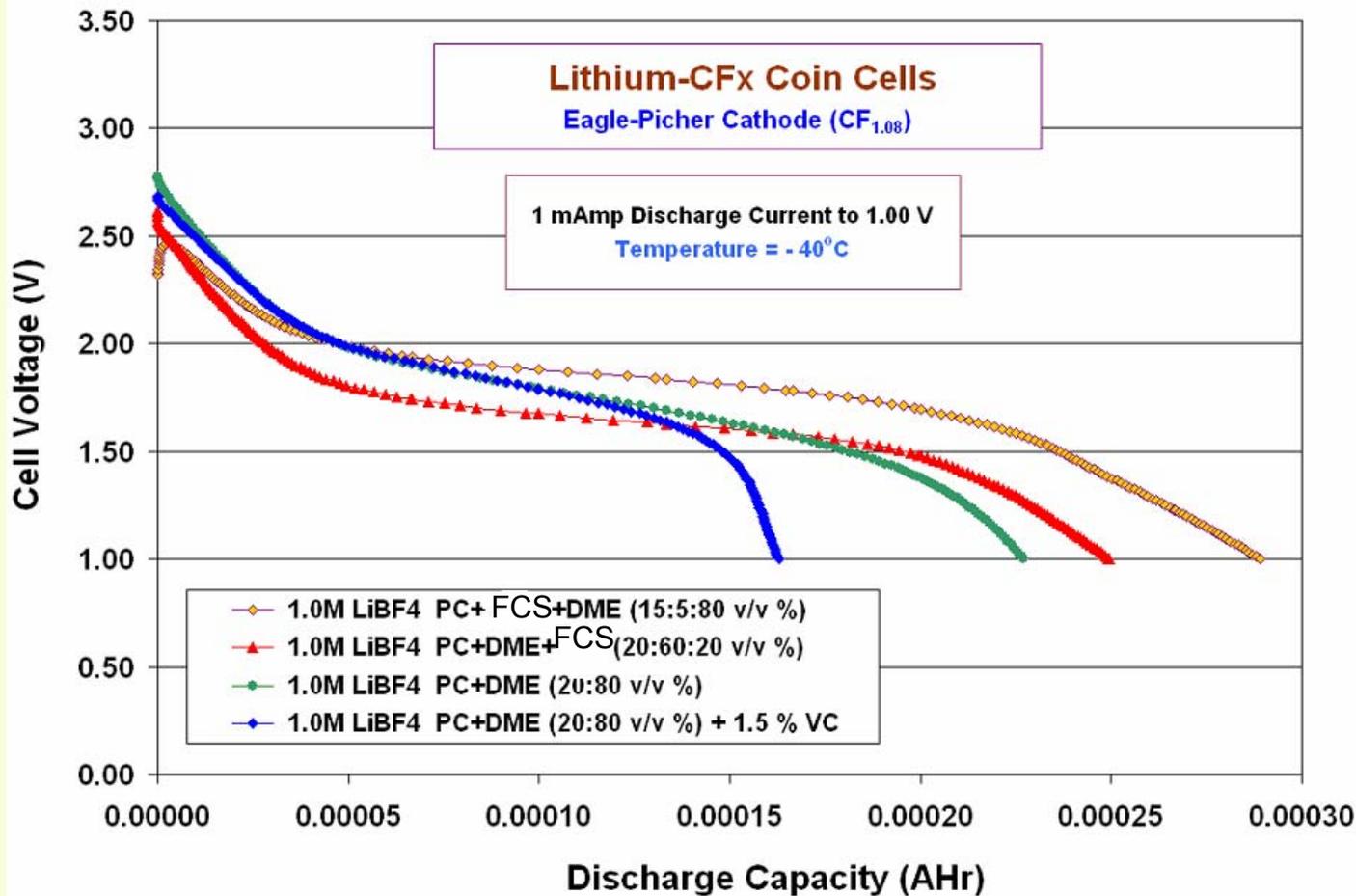


- Reduced PC content improves low temperature performance.



Comparison of Gen-2 Electrolytes at -40°C

Li-CF_x Coin cells at 1 mA & -40°C (~ C/100 Rate)



- Enhanced low temperature performance with fluorinated co-solvents.



Comparison of SOA, Gen-1, Gen-2 and Gen-3 Materials



Goals: 600 mAh/g at C/20 –Phase-1; 700 mAh/g at C/10 –Phase-2;

Cathode	Composition	Performance Summary
SOA	CF _{1.08}	• Over 700 mAh/g at rates less than C/40
Generation 1	CF ₀	• > 600 mAh/g at high rates (C/5) in thin electrodes (coin cells).
Generation-2	CF _{0.6}	• > 400 mAh/g at high rates (C/5) in thin electrodes (coin cells).
Generation-3	CF _{0.6} (nantotubes)	• Synthesized and initiated evaluation

Goals: -40°C Phase-I; -60°C- Phase-II

Electrolyte	Composition	Performance Summary
SOA	1.0 LiBF ₄ in 1:1 PC+DME	• Good for -20°C. • Good shelf life
Generation 1	1.0 LiBF ₄ in 1:4 PC+DME	• Enables operation at -40°C.
Generation-2	1.0 LiBF ₄ in • PC+FCS+DME (15:5:80 v/v %) • PC+DME+FCS (20:60:20 v/v %) • PC+DME (20:80) + 1.5 % VC	• Enables good performance at -40°C (>600 mAh/g at C/40); • Improved interfacial properties



Summary

- **Significant advances have been made in the cathodes and electrolytes for Li-ion rechargeable and Li-CF_x primary batteries**
 - **Lithium-Ion Batteries**
 - Cathodes with specific capacity exceeding 200 mAh/g, coupled with high voltage and improved thermal stability
 - Electrolytes for operations at -40 to -60°C, with reduced flammability
 - **Li-CF_x batteries**
 - Cathodes with high rate capability (>C/10), especially at low temperatures.
 - Electrolytes for enabling operations at low temperatures (-40°C).
- **Due to a shift in the focus of the Exploration Systems, this project will be considerably descoped.**
 - Li-ion effort will be absorbed into the new program
 - Li-CF_x effort will be discontinued



Acknowledgements



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